Radiolytic and Thermal Processes Relevant to Dry Storage of Spent Nuclear Fuels

(Project Number: 60392)

Principal Investigator

Dr. Steven C. Marschman
Pacific Northwest National Laboratory
P.O. Box 999, MSIN P7-27
Richland, WA 99352
(509) 376-3569 (phone)
steve.marschman@pnl.gov

Co-Investigators

Prof. Theodore E. Madey
Rutgers University, Dept. of Physics
136 Frelinghuysen Rd
Piscataway, NJ 08854-8019
(732) 445-5185 (phone)
madey@physics.rutgers.edu

Dr. Thomas M. Orlando
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K8-88
Richland, WA 99352
(509) 376-9420 (phone)
Thomas.Orlando@pnl.gov

Dr. Peter E. Haustein
Brookhaven National Laboratory
P.O. Box 5000
Upton, NY 11973
(516) 344-4340 (phone)
haustein@bnldag.ag.s.bnl.gov

Dr. James P. Cowin
Pacific Northwest National Laboratory
P.O. Box 999, MSIN K8-88
Richland, WA 99352
(509) 376-6330 (phone)
jp.cowin@pnl.gov

Collaborators

Dr. Nikolay G. Petrik, All-Russian Project and Research Institute of Complex Power
Technology, St. Petersburg

Prof. Jory Yarmoff, Dept. of Physics, University of California, Riverside

Prof. R. Dobrozemsky, Dept. of Physics, Technical University of Vienna, Austria

Specific DOE Problem

The project addresses several major DOE/EMSP science needs for the Spent Nuclear Fuel Focus Area: 1) stabilization of spent nuclear fuel, including mechanism of pyrophoricity and combustion parameters for various fuel types, 2) characterization of spent nuclear fuel, 3) development of methods to remove moisture without damage to fuel elements, and 4) characterization of corrosion, degradation, and radionuclide release mechanisms, kinetics, and rates for fuel matrices.

Research Objective

The purpose of this project is to deliver pertinent information that can be used to make rational decisions about the safety and treatment issues associated with dry storage of spent nuclear fuel materials. In particular, we will establish an understanding of: 1) water interactions with failed-fuel rods and metal-oxide materials 2) the role of thermal processes and radiolysis (solid-state and interfacial) in the generation of potentially explosive mixtures of gaseous H_2 and O_2 , and 3) the potential role of radiation-assisted corrosion during fuel rod storage.

Research Progress and Implications

Interaction of water vapor with $UO_2(001)$ was studied by using low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), low-energy ion scattering (LEIS), and electron-stimulated desorption (ESD). LEED and LEIS measurements were carried out at Rutgers University and PNNL. XPS and ESD experiments were done at the EMSL facility at PNNL. ESD measurements of clean UO_2 indicate the desorption of H^+ and O^+ ; the kinetic energy distribution of the latter peaks at 3.5 eV. The O^+ desorption threshold is at 25 eV and is correlated to the ionization of the oxygen 2s level. LEIS, XPS, and ESD results indicate that adsorbed water is completely dissociated on $UO_2(001)$ at 300K and that O atoms are incorporated into the surface. The results also suggest diffusion of oxygen into the bulk.

A high-vacuum chamber has been designed for the experiments with K-West Basin fuel samples being conducted in the radiation-controlled area of PNNL. The new facility is equipped with a low-energy (5-500 eV) electron gun, a high-resolution focused ion gun, and a secondary electron detector and mass spectrometer. This allows secondary electron microscopy imaging, secondary ion mass spectroscopy, and ESD of spent fuel samples from the K-West Basin.

Gamma radiation-induced degradation of water on oxide particle/water interfaces was studied. Thirty powdered ultrapure (>99.99%) crystal oxides were examined. According to the radiation-chemical yield, the oxides can be generally classified into three groups: 1) inhibitors, which lower the H_2 yield, 2) indifferent oxides, and 3) ZrO_2 and some other oxides that increase the H_2 yield more than the radiolysis of pure gas-phase water. A mechanism is proposed for the adsorbed water radiolysis on the ZrO_2 surface, based on the migration of excitons to the surface and their resonant coupling with the H_2O adsorption complex.

Time- and energy-resolved laser-stimulated luminescence (LSL) measurements were used to investigate the dynamics of electronic excitations in ZrO_2 . We observe LSL from the decay of three excited states, 2.70, 2.27, and 2.10 eV. The emission kinetics are hyperbolic for all the luminescence bands, which indicates a recombination mechanism. We suggest that recombination primarily involves electrons trapped at intrinsic and extrinsic defect sites and mobilized holes.

The breakdown of zirconia films (important to the integrity of Zr-alloy fuel-rod cladding) under extreme radiation conditions has been systematically studied using low-energy electron and photon bombardment of well-characterized ZrO_2 surfaces. These studies have clarified the mechanism of oxygen removal from such surfaces. This involves ionization of cation core levels, followed by interatomic auger decay resulting and rapid ejection of O^+ ions.

Planned Activities

We will submit a renewal proposal to 1) characterize major forms of water physically and chemically bonded to major components of the real SNF samples, 2) investigate radiation-induced gas generation and surface degradation on real SNF samples, cladding and rubble materials containing residual bounded water, and 3) complete the development of a predictive model for the radiolytic gas release from the surface of SNF and other components during “dry” storage.

Information Access

1997-1998 Progress Report. Available URL: <http://apollo.osti.gov/em52/1998projsum/60392.pdf>

1998-1999 Progress Report. Available URL: <http://apollo.osti.gov/em52/1998projsum/60392.pdf>

EMSP Workshop, July 1998 Project. Available: <http://apollo.osti.gov/em52/1998projsum/60392.pdf>

Haustein P. 2000. “Nuclear stimulated desorption studies of oxides relevant to spent fuel material.” *J. Nucl. Mater.* (in preparation).

Hedhili MN, BV Yakshinskiy, and TE Madey. 2000. “Interaction of water with UO_2 (001).” *Surf. Sci.* 445:512-525.

Petrik NG, AB Alexandrov, AI Vall, and TM Orlando. “Gamma radiolysis of water on oxide surfaces: Parameters controlling the energy transfer.” *J. Phys. Chem. B* (in preparation).

Petrik NG, AB Alexandrov, T.M. Orlando, and A.I. Vall. 1999. “Radiation-induced processes at oxide surfaces and interfaces relevant to spent nuclear fuel storage.” *Trans. ANS* 81,101.

Petrik NG, DP Taylor, and TM Orlando. 1999. "Laser-stimulated luminescence of yttria-stabilized cubic-zirconia crystals." *J. Appl. Phys.* 85:6770.

Shutthanandan V, S Thevuthasan, and TM Orlando. 2000. "Hydrogen-damage interactions in yttrium stabilized zirconia." *J. Nucl. Mater.* (in preparation).

Simpson WC, WK Wang, JA Yarmoff, and TM Orlando. 1999. "Photon- and electron-stimulated desorption of O⁺ from zirconia." *Surf. Sci.* 423:225.

Taylor DP, WC Simpson, K Knutsen, MA Henderson, and TM Orlando. 1998. "Photon-stimulated desorption of cations from yttria-stabilized cubic ZrO₂." *Appl. Surf. Sci.* 101:127-129.

Thevuthasan S, SI Yi, YJ Kim, TT Tran, GS Herman, V Shutthanandan, SA Chambers, CHF Peden, and TM Orlando. 2000. "Surface structure determination of Y-ZrO₂(001) using mass separated recoil spectroscopy and x-ray photoelectron diffraction." *Surf. Sci.* (in preparation).